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Quantum Theory of Inelastic Atom-Surface Scattering*

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A quantum-mechanical treatment is developed for the inelastic scattering of atoms by thermal fluctuations near a surface using Green's functions and diagrammatic methods. A basic set of equations is derived for the Green's function and T matrix by treating the thermal fluctuations, which give inelastic scattering, stochastically. This enables us to express scattering cross sections, adsorption or capture rates of atoms by the surface field, etc., in terms of a fluctuation correlation function which characterizes the surface excitations. The approach presented treats the scattering surface in a continuum approximation making it especially applicable to liquids and to solids when surface-diffraction effects are neglected. The derivation leads to a Dyson equation for the Green's function (the propagator in the presence of the fluctuating surface field) which is formally similar to the equation for the dressed-electron Green's function in the electron-phonon problem. Some essential differences exist, however, and these are discussed. The similarity between these problems is exploited to some extent to generate approximate solutions of the scattering problem to all orders in perturbation theory. The simplest case, corresponding to summing a class of diagrams with no vertex corrections, is examined. The use of separable matrix elements makes the approximation scheme particularly transparent. Expressions for the scattering and capture (adsorption) cross section are given and a resonancelike form of the cross section is shown. Results from lowest-order perturbation theory are presented for comparative purposes and their connection to previous work is described. An analogy with neutron scattering theory as formulated by Van Hove is also examined.

I. INTRODUCTION

The problem of atoms scattering from surfaces is an important one and has been receiving increased attention in the recent literature. The problem of elastic scattering of atoms by solid surfaces has been considered in detail by Lennard-Jones and co-workers in a series of papers.[1-5] They examine both the diffraction and reflection of molecular rays as well as adsorption and desorption of atoms at a solid surface. More recently, Cabrera *et al.*[6] have studied the elastic scattering problem assuming the moduli of the scattering matrix elements are small, a restriction employed in the work of Lennard-Jones *et al.*[1-5] (who use the distorted-wave Born approximation). Howsman[7] also examined elastic scattering of atoms by perfect crystals and obtained qualitative agreement with experiments.

In the study of inelastic atom-surface scattering of interest here, the solutions of the elastic-scattering problem are assumed known so that, in an inelastic event, the atom makes a transition from one eigenstate of the elastic-scattering problem to another. This is the same as the treatment of scattering from two potentials.[8] In this way, one includes transitions from free to bound states and vice versa (adsorption and desorption) as well as free-state to free-state transitions (inelastic scattering).

Cabrera, Celli, and Manson[9] examine the problem of one-phonon inelastic scattering from crystal surfaces and discuss the possible detection of surface phonons by separating out the elastic and one-phonon reflected beams. Two comprehensive reviews have been given recently by Beder[10] and Goodman.[11] To this point, all work has been aimed at atom-solid-surface interactions.

As is the case for crystalline solids, the interaction of gas atoms with the surfaces of liquids or amorphous solids provides information about the interaction forces and, as noted by Goodman,[11] provides input to many important problems in rarefied gas dynamics, such as condensation and accommodation coefficients.[12] In addition, from the differential scattering cross section, one can deduce a scattering kernel required in the evaluation of the correct hydrodynamic boundary conditions in gas dynamics,[13] including problems where evaporation and condensation on a boundary are possible.

The approach developed in this paper is based on the assumption that the scattering surface can be treated as a continuum,[14] making it especially applicable to liquids and amorphous solids. To the extent that surface-diffraction effects can be neglected (or included in an *ad hoc* manner), the theory can be used for crystalline solids. By proceeding to treat the thermal fluctuations near the surface stochastically, quantities such as transition rates, scattering cross sections, and lifetimes of specific states, can be expressed in terms of a fluctuation correlation function. The correlation function, in turn, contains characteristic information regarding the thermal fluctuations near a surface. Except for some examples, we do not consider the various forms the correlation function can have and limit ourselves to employing only its general properties, e.g., stationarity. However, it is emphasized that one can, in a separate analysis, determine the fluctuation correlation function by treating the dynamical aspects of the scattering medium in a continuum approximation.[15,16] Such an analysis would be similar to that made by Huber for thermal diffuse scattering of low-energy electrons,[17] in which the thermal motions of the atoms in the crystal are approximated by the vibrations of an isotropic elastic continuum with a stress-free surface.

It should be noted that atom capture by the surface field included in our treatment corresponds to physical adsorption, i.e., adsorption arising from the presence of van der Waals forces. The forces that give rise to chemisorption and which are related to electron sharing or electron transfer between the solid or liquid phase and the adsorbed gas atom or molecule are not included. It is assumed that the only effect of the penetration of electron orbitals of the gas atom and atoms on the surface is repulsion. In essence, therefore, the basic assumption is that the physical and chemical properties of an adsorbed atom and the surface are only slightly modified.

In the course of this treatment, some formal similarities are found between the atom-surface scattering problem and the electron-phonon problem,[18] and these are discussed in detail. In addition, the second-order results show a close analogy to the basic cross-section equation for the scattering of neutrons from a system of interacting particles. In particular, we show that the fluctuation-correlation function plays a role analogous to the generalized pair distribution function, a result that can be helpful in the interpretation of experimental results.

The structure of the remainder of the paper is the following: In Sec. II, the basic equations are derived at $T = 0$ for scalar surface displacements and then generalized to $T \neq 0$ and vector displacements. A formal analogy to the electron-phonon problem is discussed. In Sec. III, approximate solutions of the basic equations are considered and the use of separable matrix elements is examined. In Sec. IV, the inelastic scattering cross section and the adsorption and desorption cross sections are derived from expressions for a T matrix using the optical theorem. An analogy with the formulas applicable to neutron scattering from a system of interacting particles is discussed. The reduction of formulas to those from the second-order distorted-wave Born approximation is also presented. In Sec. V, simple models of the surface potential field and the fluctuation-correlation function are used to consider illustrative examples of the formalism developed in preceding sections. Specifically, the lifetime of a bound (adsorbed) state is examined in lowest-order perturbation theory. Finally, in Sec. VI, a brief summary is given.

II. SURFACE SCATTERING

Our aim in this section is to derive the basic equations for the atom Green's function (the propagator for an atom in the presence of a fluctuating surface field) and the T matrix which governs the inelastic scattering of atoms from thermal fluctuations near a surface. From the solutions of these equations, properties of physical interest, such as inelastic scattering and capture (adsorption) cross sections, can be evaluated. We will show that, under the assumptions made regarding the random time-dependent fluctuating potential field, the basic equations have a formal similarity to the coupled equations for the electron Green's function and electron self-energy that arise in the electron-phonon problem.[18]

A. $T = 0$

We begin by treating the case of a surface at $T = 0$ to simplify and make clear the derivation of the necessary equations. The generalization to finite temperatures is carried out in Sec. II B following the formalism outlined by Abrikosov *et al.*[19] We want to calculate the inelastic scattering of atoms by thermal fluctuations near a surface, which shall be treated stochastically. This makes our treatment in some ways formally similar to methods of evaluating the electrical conductivity in metals[20] or the surface conductivity in a semiconductor,[21] where one treats the problem of a random set of scatterers (e.g., impurities). However, the unperturbed Hamiltonian, which includes the mean surface field, is different, and the Green's function is a true single-particle Green's function (propagator for the atom). Further similarities and differences between this and other problems will be discussed as we proceed.

1. Basic Hamiltonian and Green's Functions

To derive the basic equations, we write the Hamiltonian for an atom in the presence of the surface field as

$$H = H_0(z) + H_a + H_1(\vec{r}) , \tag{1}$$

where H_a is the Hamiltonian of the adsorbate and $H_1(\vec{r})$ is the perturbing potential. z denotes the coordinate perpendicular to the scattering surface, and the equilibrium location of the surface is the plane $z = 0$. We will treat the surface in a continuum approximation[14] and consider the atom to be in the half-space $z > 0$. Thus, the unperturbed particle Hamiltonian H_0 includes the average potential field of the surface, $V_0(z)$, and depends only on z in the continuum approximation.

Under these conditions, the eigenfunctions of H_0 have the form

$$\psi_{\vec{k},\nu}(\vec{r}) = c\, e^{i\vec{k}\cdot\vec{x}} \varphi_\nu(z) , \tag{2}$$

where $\vec{r} = \vec{x} + \vec{z}$ and $\vec{x}$ is a vector in the surface while $\vec{z}$ is perpendicular to the surface. The vector $\vec{k}$ is a wave vector parallel to the surface, and the index ν labels the $\vec{z}$ quantum states. The $\varphi_\nu(z)$ are eigenfunctions satisfying

$$(H_0)_z\, \varphi_\nu(z) = [p_z^2/2M + V_0(z)]\, \varphi_\nu(z) = \nu \varphi_\nu(z) , \tag{3}$$

and the total energy is

$$\mathcal{E}_{\vec{k},\nu} = \vec{k}^2/2M + \nu . \tag{4}$$

Here, M is the mass of the atom.

In terms of the $\psi_{\vec{k},\nu}(\vec{r})$, the "free"-atom Green's function [corresponding to H_0, which includes $V_0(z)$, the mean surface field] is given by $[m \equiv (\vec{k}, \nu)]$

$$G^0(\vec{r}', \vec{r}; \mathcal{E}) = \sum_m \frac{\psi_m(\vec{r})\, \psi_m^\dagger(\vec{r}')}{\mathcal{E} - \mathcal{E}_m + i\epsilon} . \tag{5}$$

Thus, in Fourier space $[(\vec{k}, \nu)$ space$]$, the free-atom propagator is

$$G_m^0(\mathcal{E}) = 1/(\mathcal{E} - \mathcal{E}_m + i\epsilon) . \tag{6}$$

Note that the eigenvalue spectrum in ν is continuous for $\nu > 0$ and discrete for $\nu < 0$, and the discrete states correspond to states for atoms adsorbed onto the surface. The normalization of the ν states is taken as

$$\int_0^\infty \varphi_{\nu'}^*(z)\, \varphi_\nu(z)\, dz = \delta_{\nu\nu'} , \tag{7}$$

and we assume that the surface is impenetrable by setting $\varphi_\nu(0) \equiv 0$. The actual form of $\varphi_\nu(z)$ depends on the choice of $V_0(z)$ and will not be considered in detail here. Suffice it to say that in detailed computations, one may adopt the form

$$V_0(z) \propto -(1/z^3 - 1/z^9) , \tag{8}$$

which can be derived from the Lennard-Jones (6-12) potential by integrating over $\vec{x}$, [22,23] or one can use the Morse potential.[1,23] Lennard-Jones and Strachan[1] have evaluated the ν eigenvalues and eigenfunctions for the Morse potential, and these were, in fact, used by Cabrera *et al.*[6] in their recent detailed treatment of elastic scattering from solid surfaces. In summary, then, the average surface potential $V_0(z)$ is included in the "unperturbed" Hamiltonian H_0, and the eigenfunctions $\varphi_\nu(z)$ are assumed known.

The quantity of basic interest is the Green's function for a particle in the presence of the external perturbing potential, which will be called the dressed-atom Green's function. Let $\delta R(\vec{x})$ denote the deviation of the surface from its equilibrium position at $z = 0$ and for the moment assume $\delta R(\vec{x})$ is in the z direction. The generalization to vector displacement operators $\delta \vec{R}$ will be done in Sec. II B. In the Heisenberg picture, the fluctuation operator defined through

$$\delta R(\vec{x}, t) = e^{iH_a t}\, \delta R(\vec{x})\, e^{-iH_a t} \tag{9}$$

depends on the position on the surface $\vec{x}$ and the time t. The first step is to expand the fluctuating potential field as a power series in $\delta R(\vec{x})$:

$$V(z, \delta R(\vec{x})) = V_0(z) + V^{(1)}(z)\, \delta R(\vec{x}) + \frac{V^{(2)}(z)}{2!}\, \delta R^2(\vec{x}) + \cdots . \tag{10}$$

The bracketed superscript on $V^{(n)}(z)$ represents the nth-order derivative, and $V_0(z)$ is, as before, the mean potential field of the surface. It is shown in the Appendix that by making a renormalized harmonic approximation, this series can be summed with the effect that the coefficient of $\delta R(\vec{x})$ becomes a temperature-dependent function $V_1(z, T)$. In other words, we consider a renormalized vertex and are not restricted to small displacements (see the Appendix). The total system Hamiltonian, in the Heisenberg picture, for an atom in the presence of a time-dependent fluctuating field, thus becomes

$$\mathcal{H} = H_0 + \mathcal{H}_1(\vec{r}, t) , \tag{11}$$

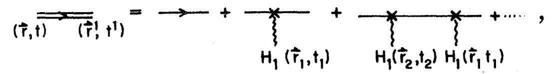
where

$$\mathcal{H}_1(\vec{r}, t) = V_1(z, T)\, \delta R(\vec{x}, t) . \tag{12}$$

To derive an expression for the dressed-atom Green's function, consider first the usual perturbation theory expansion for a particle in an external time-dependent perturbing field.[19] It is

$$G(\vec{r}', \vec{r}; t', t) = G_0(\vec{r}', \vec{r}, t' - t) + \int_{t < t_1 < t'} G_0(\vec{r}', \vec{r}_1, t' - t_1) \mathcal{H}_1(\vec{r}_1, t_1)\, G_0(\vec{r}_1, \vec{r}, t_1 - t)\, d\vec{r}_1\, dt_1$$
$$+ \int_{t < t_2 < t_1 < t'} d\vec{r}_1\, d\vec{r}_2\, dt_1\, dt_2\, G_0(\vec{r}', \vec{r}_1, t' - t_1) \mathcal{H}_1(\vec{r}_1, t_1)\, G_0(\vec{r}_1, \vec{r}_2, t_1 - t_2) \mathcal{H}_1(\vec{r}_2, t_2)\, G(\vec{r}_2, \vec{r}, t_2 - t) + \cdots , \tag{13a}$$

or, simply,



(13b)

where the double line represents the dressed-atom Green's function G, the single lines correspond to free-atom propagators G_0 (atoms in the presence of the mean surface field only), and the crosses with wavy lines denote the action of the perturbing field $\mathcal{H}_1(\vec{r}, t)$. At nth order, there are n products of the fluctuation operator $\delta R(\vec{x}, t)$, together with $(n+1)$ intermediate-state Green's functions from the elastic scattering problem.

2. *Stochastic Perturbing Potential; Averaged Green's Functions and Dyson Equation*

The thermal fluctuations which give inelastic scattering will be treated stochastically. This means we consider $\delta R(\vec{x}, t)$ as a random time-dependent fluctuation operator, and we will assume that it is described by a Gaussian random process (i.e., only pair correlations are retained). This means the ensemble average of a fluctuation operator is zero;

$$\langle \delta R \rangle = (Z)^{-1} \operatorname{tr}(e^{-\beta H_a} \delta R) = 0 \ , \tag{14}$$

where Z is the trace over the density operator of the system from which we are scattering,

$$Z = \operatorname{tr}(e^{-\beta H_a}) \ , \tag{15}$$

and β is $(1/k_B T)$.

The ensemble average of a pair defines a pair correlation function $D(\vec{x}_1, \vec{x}_2; t_1, t_2)$ as

$$\langle \delta R(\vec{x}_1, t_1)\, \delta R(\vec{x}_2, t_2) \rangle = Z^{-1} \operatorname{tr}[e^{-\beta H_a} \delta R(\vec{x}_1, t_1) \times \delta R(\vec{x}_2, t_2)] \equiv D(\vec{x}_1, \vec{x}_2; t_1, t_2) \ . \tag{16}$$

For the case of $T = 0$, we take the limit of these expressions as $\beta \to \infty$.

Furthermore, the average of higher-order products of fluctuation operators are expressed in terms of pair correlations and the average value. Because $\langle \delta R \rangle = 0$, all odd-order products are zero, and even-order products become

$$\begin{aligned} &\langle \delta R(\vec{x}_1, t_1) \cdots \delta R(\vec{x}_{2n}, t_{2n}) \rangle \\ &\quad = \langle \delta R(\vec{x}_1, t_1)\, \delta R(\vec{x}_2, t_2) \rangle \langle \delta R(\vec{x}_3, t_3)\, \delta R(\vec{x}_4, t_4) \rangle \cdots \\ &\qquad \times \langle \delta R(\vec{x}_{2n-1}, t_{2n-1})\, \delta R(\vec{x}_{2n}, t_{2n}) \rangle \\ &\qquad\qquad + \text{all possible permutations} \ , \end{aligned} \tag{17}$$

keeping in mind that $\langle AB \rangle = \langle BA \rangle$. Finally, using time-translation invariance (stationarity) and the assumption of a spatially homogeneous scattering surface, the correlation between pairs depends only on the difference of its variables,

$$\langle \delta R(\vec{x}_i, t_i)\, \delta R(\vec{x}_j, t_j) \rangle = D(\vec{x}_j - \vec{x}_i; t_j - t_i) \ . \tag{18}$$

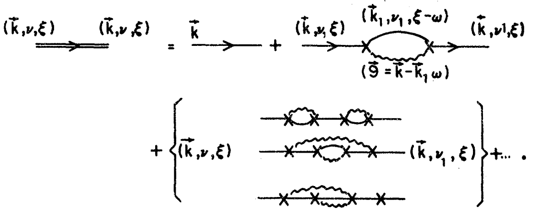
$D(\vec{x}_j - \vec{x}_i; t_j - t_i)$ is the pair-fluctuation-correlation function.

A series expansion can now be derived for an average dressed-atom Green's function by performing an ensemble average over the fluctuations operators term by term to infinite order in the perturbation series [Eq. (13)]. The "free"-atom Green's function $G_0(\vec{r}', \vec{r}, t' - t)$ is unaffected by an ensemble average that involves $e^{-\beta H_a}$. The resulting series is

$$\begin{aligned} \bar{G}(\vec{r}', \vec{r}; t' - t) &= G_0(\vec{r}', \vec{r}, t' - t) \\ &\quad + \int dr_1\, dr_2\, G_0(\vec{r}' - \vec{r}_2, t' - t_2)\, G_0(\vec{r}_2 - \vec{r}_1, t_2 - t_1) \\ &\qquad \times D(\vec{x}_2 - \vec{x}_1, t_2 - t_1)\, G_0(\vec{r}_1 - \vec{r}, t_1 - t) \\ &\qquad\quad + (\text{three fourth-order terms}) + \cdots \ , \end{aligned} \tag{19}$$

where $\bar{G}$ denotes an averaged dressed-atom Green's function.

Diagrammatically, the effect of the averaging procedure is to connect the wavy lines and vertex points in Eq. (13b) and to associate with each connecting wavy line a fluctuation propagator or, at $T = 0$, simply the pair-fluctuation-correlation function. In $(\vec{k}, \nu)$ space, the $\vec{k}$ states are preserved ($\vec{k}$ is the atom wave vector parallel to the scattering surface), but the ν states are not; so the series becomes



(20)

With each wavy line, one can associate a fluctuation propagator, defined at $T = 0$ by

$$iP(\vec{q}, \omega) = \int_0^\infty \frac{d\xi}{2\pi}\, D(\vec{q}, \xi)\, \frac{1}{\omega - \xi + i\delta} \ , \tag{21}$$

where $\vec{q} = \vec{k} - \vec{k}_1$, and $D(\vec{q}, \xi)$ is the space-time Fourier transform of the fluctuation-correlation function

$$D(\vec{q}, \xi) = \int d\tau\, d\vec{x}\, e^{i(\vec{q}\cdot\vec{x} - \xi\tau)} D(\vec{x}, \tau) \ . \tag{22}$$

If we make use of the definitions of the free-atom Green's functions, Eqs. (5) and (6), then the following rules allow one to write out the series for the dressed-atom Green's function explicitly in Fourier space. First, one associates with each vertex (cross) the matrix element $M_{\nu_j \nu_i}(T)$ defined by

$$M_{\nu_j \nu_i}(T) = \int dz\, \varphi^*_{\nu_j}(z)\, V_1(z, T)\, \varphi_{\nu_i}(z) \ , \tag{23}$$

where the $\varphi_{\nu_i}(z)$ are known eigenfunctions of H_0. Second, with each wavy line is associated the fluctuation propagator $P(\vec{q}, \omega)$. Third, each single line denotes a free-atom propagator as given by Eq. (6). Finally, carry out the sums over intermediate-state variables. A double line represents the averaged dressed-atom Green's function. Thus, defining $\kappa = (\vec{k}, \mathcal{E})$, the series (20) is

$$\overline{G}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa)\,\delta_{\nu\nu'} + G^0_{\nu'}(\kappa) \sum_{\vec{k}_1, \nu_1} M_{\nu'\nu_1} M_{\nu_1\nu} \int d\omega \times G^0_{\nu_1}(\vec{k}_1, \mathcal{E} - \omega)\, P(\vec{q}, \omega)\, G^0_\nu(\kappa) + \cdots . \tag{24}$$

This is the basic series expansion for the dressed-atom Green's function and is fundamental to our treatment of inelastic atom-surface scattering.

The result of retaining only the leading two terms in the expansion (24) is the distorted-wave Born approximation (DWBA) used by Lennard-Jones and co-workers.[1-5] Cabrera, Celli, and Manson[9] also used it to illustrate results of their more detailed treatment of inelastic atom-surface scattering.

Such results will be valid only in the limit of "weak" coupling between the incident atom and the fluctuating surface field. In other cases, it is necessary, as in many-body theory,[19] to investigate the remaining terms in the series (24) and sum at least certain classes of diagrams to infinite order in perturbation theory. Diagram summation leads to the Dyson equation for the dressed-atom Green's function.

The derivation of the Dyson equation for $\overline{G}_{\nu'\nu}(\kappa)$ can be carried out in a standard way.[19] The result is

(25a)

$$\overline{G}_{\nu'\nu}(\kappa)\, G^0_\nu(\kappa)\, \xi_{\nu\nu'} + G^0_{\nu'}(\kappa) \sum_{\nu'} K_{\nu'\nu_1}(\kappa)\, G_{\nu_1\nu}(\kappa) , \tag{25b}$$

where

(26a)

$$K_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2, \nu_2, \nu_2'} M_{\nu'\nu_2'} \int d\omega\, G_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) \times P(q, \omega)\, \Gamma_{\nu_2\nu_1}(\vec{k}, \vec{k}_2, \mathcal{E}, \omega), \tag{26b}$$

and

$$\oslash \equiv \Gamma_{\nu_2\nu_2}(\vec{K}, \vec{K}, \xi, \omega). \tag{27}$$

The vertex function $\Gamma_{\nu_2\nu_1}(\vec{k}, \vec{k}_2, \mathcal{E}, \omega)$ accounts for all diagrams with fluctuation lines that cross.

Equations (25) and (26) constitute the basic equations for the inelastic scattering of atoms by thermal fluctuations at a surface. In short, they have been derived by treating the surface in a continuum approximation and assuming that the random time-dependent fluctuating perturbing field can be described as a Gaussian random process.

A formal similarity between this problem and the electron-phonon problem[19,24,25] is made clear by examining the diagrammatic equation for the atom Green's function $\overline{G}_{\nu'\nu}(\kappa)$. The fluctuation propagator $P(\vec{q}, \omega)$ is analogous to the phonon propagator, while the atom Green's function plays the role of the dressed-electron propagator. The K function is like the electron self-energy. An essential difference between these problems exists, however, because the fluctuation-correlation function $D(\vec{q}, \omega)$, from which we determine $P(\vec{q}, \omega)$, is regarded as *given* in the atom-surface scattering problem. Thus, processes corresponding to phonon self-energies can be neglected, and $D(\vec{q}, \omega)$ alone contains the characteristic information about the thermal fluctuations near a surface.

For completeness, the T-matrix equation will be given for later use. In terms of the atom Green's function, it is

$$T_{\nu'\nu}(\kappa) = K_{\nu'\nu}(\kappa) + \sum_{\nu_1, \nu_2} K_{\nu'\nu_2}(\kappa)\, \overline{G}_{\nu_2\nu_1}(\kappa)\, K_{\nu_1\nu}(\kappa) \tag{28}$$

or, equivalently,

$$T_{\nu'\nu}(\kappa) = K_{\nu'\nu}(\kappa) + \sum_{\nu_1} T_{\nu'\nu_1}(\kappa)\, G^0_{\nu_1}(\kappa)\, K_{\nu_1\nu}(\kappa) . \tag{29}$$

In the usual way,[26] expressions for the inelastic scattering cross sections and lifetimes can be calculated once $T_{\nu'\nu}(\kappa)$ is known.

B. $T \neq 0$

By analogy with the finite-temperature generalization procedure of results at $T = 0$ in statistical physics,[19,27] the Dyson equation (25) at finite temperatures is derived by replacing $\mathcal{E}$ by $i\mathcal{E}_n$, where $i\mathcal{E}_n = (2n+1)\pi i/\beta$, and replacing

$$\int_{-\infty}^{\infty} d\omega \to \frac{2\pi i}{\beta} \sum_{n=-\infty}^{\infty} \equiv \frac{2\pi i}{\beta} \sum_{\omega_n} . \tag{30}$$

Equation (26) at $T \neq 0$ becomes

$$K_{\nu'\nu}(\vec{k}, i\mathcal{E}_n) = \sum_{\vec{k}_2, \nu_2, \nu_2'} M_{\nu'\nu_2'} \sum_{\omega_n} \frac{2\pi i}{\beta}\, \overline{G}_{\nu_2'\nu_2}(\vec{k}_2, i\omega_n) \times P(\vec{q}, i(\mathcal{E}_n - \omega_n))\, \Gamma_{\nu_2\nu_1}(\vec{k}, \vec{k}_2, i\mathcal{E}_n, i\omega_n) , \tag{31}$$

and Eq. (25) becomes

$$\overline{G}_{\nu'\nu}(\vec{k}, i\mathcal{E}_n) = G^0_\nu(\vec{k}, i\mathcal{E}_n)\,\delta_{\nu\nu'} + G^0_\nu(\vec{k}, i\mathcal{E}_n) \times \sum_{\nu_1} K_{\nu'\nu_1}(\vec{k}, i\mathcal{E}_n)\, \overline{G}_{\nu_1\nu}(\vec{k}, i\mathcal{E}_n) . \tag{32}$$

Similarly, the T-matrix equation is

$$T_{\nu'\nu}(\vec{k}, i\mathcal{E}_n) = K_{\nu'\nu}(\vec{k}, i\mathcal{E}_n) + \sum_{\nu_1} T_{\nu'\nu_1}(\vec{k}, i\mathcal{E}_n) \times G^0_{\nu_1}(\vec{k}, i\mathcal{E}_n)\, K_{\nu_1\nu}(\vec{k}, i\mathcal{E}_n) . \tag{33}$$

In evaluating this T matrix at finite temperature, one uses the "retarded" K matrix and free Green's function obtained by the analytic continuation $i\mathcal{E}_n \to \mathcal{E} + i\delta$.

As an illustration of these results, consider the

T matrix in the second-order Born approximation. Following the procedure outlined by Schrieffer,[18] one can derive (letting $i\mathcal{E}_n \to \mathcal{E} + i\delta$)

$$T_{\nu'\nu}(\vec{k}, \mathcal{E}) = \sum_{\vec{k}_1, \nu_1} M_{\nu'\nu_1} M_{\nu_1\nu} \int_0^\infty d\xi\, D(\vec{q}, \xi) \times \left(\frac{1+b(\xi)}{\mathcal{E} - \mathcal{E}_{k_1,\nu_1} - \xi + i\delta} + \frac{b(\xi)}{\mathcal{E} - \mathcal{E}_{\vec{k}_1,\nu_1} + \xi + i\delta} \right) . \tag{34}$$

The functions $b(\xi)$ are the Bose factors ($\beta = 1/k_B T$)

$$b(\xi) = (e^{\beta\xi} - 1)^{-1} , \tag{35}$$

so that the term in (34) involving $1 + b(\xi)$ corresponds to fluctuation creation interactions, while that containing $b(\xi)$ accounts for fluctuation annihilations. In the limit that $T \to 0$, the factor $b(\xi) \to 0$, and we recover the $T = 0$ result:

$$T_{\nu'\nu}(\vec{k}, \mathcal{E}) = \sum_{\nu_1} M_{\nu'\nu_1} M_{\nu_1\nu} \int_0^\infty d\xi\, D(\vec{q}, \xi) \times \frac{1}{\mathcal{E} - \mathcal{E}_{\vec{k}_1,\nu_1} + \xi + i\delta} . \tag{36}$$

This includes only fluctuation creation terms, as it should. In addition, the T matrix in Eq. (34) is the same as would be derived in the DWBA.

C. Vector Displacement Operator

The generalization to vector fluctuation operators $\delta\vec{R}(\vec{x}_i, t_i)$ is performed by defining $\vec{r} \equiv \vec{z} + \delta\vec{R}$ and expressing $\mathcal{H}_1(\vec{r}, t)$ in terms of an expansion of $V(\vec{r})$, as in Eq. (10). Let V_α denote the derivative with respect to α (α represents, in Cartesian coordinates, x, y, or z) and $V_\alpha(z)$ recalls that the coefficient of $\delta\vec{R}(\vec{x}_i, t_i)$ is local. Thus $V(\vec{r})$ is expressed by the expansion

$$V(\vec{r}) = V_0(z) + V_\alpha(z)\, \delta R_\alpha(\vec{x}, t) \tag{37}$$

and

$$\mathcal{H}_1 = V_\alpha(z)\, \delta R_\alpha(\vec{x}, t) . \tag{38}$$

Repeated indices signify summation. As before, assume that $\delta\vec{R}$ characterizes a generalized Gaussian random process expressed by the properties

$$\langle \delta R_\alpha \rangle = 0 , \tag{39}$$

$$\langle \delta R_\alpha(\vec{x}_i, t_i)\, \delta R_\beta(\vec{x}_j, t_j) \rangle = D_{\alpha\beta}(\vec{x}_j - \vec{x}_i, t_j - t_i) , \tag{40}$$

with all higher-order correlations expressible in terms of pair correlations:

$$\langle \delta R^1_\alpha\, \delta R^2_\beta \cdots \delta R^{2n-1}_\gamma \rangle = 0, \quad n = 1, 2, \ldots \tag{41}$$

$$\langle \delta R^1_\alpha\, \delta R^2_\beta \cdots \delta R^{2n}_\gamma \rangle = \langle \delta R^1_\alpha\, \delta R^2_\beta \rangle \cdots \langle \delta R^{2n-1}\, \delta R^{2n}_\gamma \rangle + \text{all permutations} . \tag{42}$$

The superscript on δR^i_α denotes $\delta R_\alpha(\vec{x}_i, t_i)$. The brackets $\langle \cdots \rangle$ again signify $\mathrm{tr}(e^{-\beta H_a}\, \delta R^1_\alpha\, \delta R^2_\beta)/Z$ and

$$\langle \delta R^1_\alpha\, \delta R^2_\beta \rangle = \langle \delta R^2_\beta\, \delta R^1_\alpha \rangle . \tag{43}$$

Define the tensor correlation function

$$\overleftrightarrow{D}^{ij} \equiv \overleftrightarrow{D}^{ij}(\vec{x}_i - \vec{x}_j, t_i - t_j) \equiv (D^{ij}_{\alpha\beta}) \tag{44}$$

and the vector

$$\partial\vec{V}(z) = (V_\alpha(z)) . \tag{45}$$

In terms of $\overleftrightarrow{D}^{ij}$ and $\partial\vec{V}$, a tensor propagator and a vector matrix element can be defined:

$$i\overleftrightarrow{P}^{ij}(\vec{k}, \omega) = \int_0^\infty \frac{d\xi}{2\pi}\, \overleftrightarrow{D}^{ij}(\vec{k}, \xi) \times \left(\frac{1}{\omega - \xi + i\delta} - \frac{1}{\omega + \xi - i\delta} \right) , \tag{46}$$

$$\vec{M}_{\nu'\nu} \equiv \langle \varphi_{\nu'} | \partial\vec{V} | \varphi_\nu \rangle . \tag{47}$$

With these definitions, the generalized Dyson equation becomes

$$\overline{G}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa)\, \delta_{\nu\nu'} + G^0_{\nu'}(\kappa) \sum_{\nu_1} K_{\nu'\nu_1}(\kappa)\, \overline{G}_{\nu_1\nu}(\kappa) \tag{48}$$

and

$$K_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2, \nu_2, \nu_2'} \vec{M}^T_{\nu'\nu_2'} \int d\omega\, \overline{G}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) \times \overleftrightarrow{P}^{21}(\vec{q}, \omega)\, \Gamma_{\nu_2\nu_1}(\vec{k}_1, \vec{k}_2, \mathcal{E}, \omega) . \tag{49}$$

The function $\vec{\Gamma}_{\nu_2\nu_1}(\vec{k}_1, \vec{k}_2, \mathcal{E}, \omega)$ represents a generalized vector vertex function and, in the simplest approximation, is replaced by $\vec{M}_{\nu_2\nu_1}$.

D. Section Summary

In this section, we have derived the basic series expansion for the atom Green's function and, from this, a Dyson equation. We have presented general results for $T \neq 0$ and for vector displacements, as well as specific equations at $T = 0$ and for scalar surface displacements. We have also demonstrated a formal similarity between these equations and the equations for the dressed-electron Green's function and self-energy in the electron-phonon problem and pointed out essential differences which exist. To proceed further, we now turn to methods for approximately solving for the atom Green's function and the T matrix. These can then be related to inelastic scattering cross sections and adsorption and emission rates of physical interest.

III. APPROXIMATE SOLUTIONS OF THE DYSON EQUATION

A. Iteration on the K Matrix

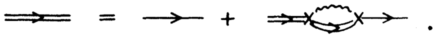
The simplest approximate solution for the atom Green's function is obtained by retaining diagrams where only one fluctuation exists at a given time. This means we neglect higher-order vertex corrections and approximate the vertex function by the equation

$$\Gamma_{\nu_2\nu_1}(\vec{k}_1, \vec{k}_2, \mathcal{E}, \omega, T) \simeq M_{\nu_2\nu_1}(T) . \tag{50}$$

The K-matrix equation now becomes

$$K_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2,\nu_2,\nu_2'} M_{\nu'\nu_2'} \int \overline{G}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) \times P(\vec{q}, \omega) M_{\nu_2\nu_1}\, d\omega \,, \qquad (51)$$

and the Dyson equation is



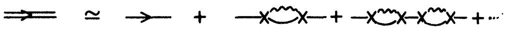
(52)

Both Eqs. (51) and (52) correspond to an approximation which includes multifluctuation contributions but neglects vertex corrections.

An approximation scheme can be generated by iterating in $\overline{G}$ on the K matrix. If we approximate the dressed-atom Green's function by the free Green's function in the K-matrix equation,

$$K_{\nu'\nu_1}(\kappa) \simeq K^{(1)}_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2,\nu_2} M_{\nu'\nu_2} M_{\nu_2\nu_1} \int d\omega \times G^0_{\nu_2}(\vec{k}_2, \mathcal{E} - \omega) P(\vec{q}, \omega) \,, \qquad (53)$$

a "one-fluctuation" approximation is obtained which sums the series



(54)

and leads to an integral equation in ν for $\overline{G}_{\nu'\nu}(\kappa)$ $[\equiv \overline{G}^{(1)}_{\nu'\nu}(\kappa)]$:

$$\overline{G}^{(1)}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa)\,\delta_{\nu\nu'} + G^0_{\nu'}(\kappa) \sum_{\nu_1} K^{(1)}_{\nu'\nu_1}(\kappa)\, \overline{G}^{(1)}_{\nu_1\nu}(\kappa) \,. \qquad (55)$$

Here $K^{(1)}_{\nu'\nu_1}(\kappa)$ is the kernel of the integral equation. The first iteration on $\overline{G}^{(1)}_{\nu'\nu}(\kappa)$ gives the second-order DWBA.

A hierarchy of solutions can be producted by successively iterating on the K matrix, and the ith iteration will include ith-order fluctuation processes. For example, two-fluctuation processes are included by solving

$$\overline{G}^{(2)}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa) + G^0_{\nu'}(\kappa) \sum_{\nu_1} K^{(2)}_{\nu'\nu_1}(\kappa) \overline{G}^{(2)}_{\nu_1\nu}(\kappa) \,, \qquad (56)$$

where

$$K^{(2)}_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2,\nu_2,\nu_2'} M_{\nu'\nu_2'} M_{\nu_2\nu_1} \int d\omega \times \overline{G}^{(1)}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) P(\vec{q}, \omega) \,. \qquad (57)$$

In general, at ith order, the Dyson equation is

$$\overline{G}^{(i)}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa) + G^0_{\nu'}(\kappa) \sum_{\nu_1} K^{(i)}_{\nu'\nu_1}(\kappa) \overline{G}^{(i)}_{\nu_1\nu}(\kappa) \qquad (58)$$

and

$$K^{(i)}_{\nu'\nu_1}(\kappa) = \sum_{\vec{k}_2,\nu_2,\nu_2'} M_{\nu'\nu_2'} M_{\nu_2\nu_1} \int_{-\infty}^{\infty} d\omega \times \overline{G}^{(i-1)}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) P(\vec{q}, \omega) \,. \qquad (59)$$

B. Separated-Kernel (Pincherle-Goursat) Approximation

Equation (52) is an inhomogeneous integral equation that can be solved by iteration [as mentioned, the first iteration on $\overline{G}^{(1)}_{\nu'\nu}(\kappa)$ gives the second-order Born approximation], but a closed-form solution is, in general, difficult. As is well known, a closed-form solution is possible if $K_{\nu'\nu}(\kappa)$ is a Pincherle-Goursat[28] (PG) or separated kernel:

$$K_{\nu'\nu}(\kappa) = \sum_{i=1}^{N} X_i(\nu, \kappa) Y_i(\nu', \kappa) = Y^T(\nu', \kappa) \cdot X(\nu, \kappa) \,, \qquad (60)$$

where $X \equiv (X_i)$ and $Y \equiv (Y_i)$ are column vectors and the superscript T denotes transpose. The solution for $\overline{G}_{\nu'\nu}(\kappa)$ is

$$\overline{G}_{\nu'\nu}(\kappa) = G^0_\nu(\kappa)\delta_{\nu\nu'} + G^0_{\nu'}(\kappa) Y^T(\nu', \kappa) \cdot (\underline{I} - \underline{B})^{-1} \cdot X(\nu, \kappa) G^0_\nu(\kappa) \,, \qquad (61)$$

where $\underline{I}$ is the identity matrix and $\underline{B}(\kappa)$ is a matrix defined by

$$\underline{B}(\kappa) = \sum_{\nu'} X(\nu', \kappa) \cdot Y^T(\nu', \kappa) G^0_{\nu'}(\kappa) \,. \qquad (62)$$

The solutions of

$$\det[\underline{I} - \underline{B}(\kappa)] = 0 \qquad (63)$$

are eigenvalues of H, while zeros of

$$\det(\mathrm{Re}[\underline{I} - \underline{B}(\kappa)]) = 0 \qquad (64)$$

will act as resonance points for the inelastic scattering cross section. This will be discussed in more detail in Secs. IV and V.

A kernel like (54) is generated by assuming a PG expansion (of finite rank) of the matrix elements $M_{\nu_2\nu_1}$:

$$M_{\nu_2\nu_1} = \langle \varphi_{\nu_2} | V_1 | \varphi_{\nu_1} \rangle = \sum_{i=1}^{N} a_i(\nu_1) a_i^*(\nu_2) = a^T(\nu_1) \cdot a^*(\nu_2) \,, \qquad (65)$$

where $a \equiv (a_i)$ is a column vector. Then,

$$K_{\nu'\nu_1}(\kappa) = \sum_{\nu_2\nu_2'} \left(\sum_{i,j}^{N} a_i(\nu_1) a_i^*(\nu_2) a_j(\nu_2') a_j^*(\nu') \right) \times \int d\vec{k}_2\, d\omega\, \overline{G}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) P(\vec{q}, \omega) \,. \qquad (66)$$

Letting

$$A_{ji}(\kappa) \equiv \sum_{\nu_2\nu_2'} a_i^*(\nu_2) \int d\vec{k}_2\, d\omega\, \overline{G}_{\nu_2'\nu_2}(\vec{k}_2, \mathcal{E} - \omega) \times P(\vec{q}, \omega) a_j(\nu_2') \,, \qquad (67)$$

$$\underline{A}(\kappa) = (A_{ji}(\kappa)) \,, \qquad (68)$$

$$K_{\nu'\nu_1}(\kappa) = a^{*T}(\nu') \cdot \underline{A}(\kappa) \cdot a(\nu_1) \,. \qquad (69)$$

Thus, we can define X and Y via

$$X(\nu_1, \kappa) = a(\nu_1) \,, \qquad (70)$$

$$Y^T(\nu', \kappa) = a^*(\nu')^T \cdot \underline{A}(\kappa) \,, \qquad (71)$$

so that $\underline{B}(\kappa)$ becomes

$$\underline{B}(\kappa) = \underline{C}^0(\kappa) \cdot \underline{A}(\kappa) \,, \qquad (72)$$

where

$$\underline{C}^0(\kappa) \equiv \sum_{\nu'} a(\nu') \cdot a^*(\nu')^T G^0_{\nu'}(\kappa) \,. \tag{73}$$

The solution for $\overline{G}_{\nu'\nu}(\kappa)$ is again given by Eq. (61) using the definitions (70)–(72).

Now, however, one can determine an integral equation for the K matrix or, equivalently, for $\underline{A}(\kappa)$, namely,

$$\underline{A}(\kappa) = \int d\vec{k}_2 \, d\omega \, P(\vec{q}, \omega) \left[\underline{I} - \underline{A}(\vec{k}_2, \mathcal{E} - \omega) \cdot \underline{C}^0(\vec{k}_2, \mathcal{E} - \omega)\right]^{-1} \cdot \underline{C}^0(\vec{k}_2, \mathcal{E} - \omega) \,. \tag{74}$$

Successive iterations on the A matrix in the integrand, beginning with $\underline{A}^{(0)} = \underline{0}$, the null matrix, generates the one-fluctuation approximation, two-fluctuation approximation, etc.

The simplest example to carry out in any detail is the scalar case of a factorizable matrix element (rank 1):

$$M_{\nu_2\nu_1} = a_1(\nu_1) a_1^*(\nu_2) \,. \tag{75}$$

With the definitions (paralleling the previous discussion in notation)

$$C^0(\kappa) = \sum_{\nu} a_1(\nu) \, G^0_\nu(\kappa) a_1^*(\nu) \,, \tag{76}$$

$$C(\kappa) = \sum_{\nu_2\nu_2'} a_1^*(\nu_2) \overline{G}_{\nu_2'\nu_2}(\kappa) a_1(\nu_2') \,, \tag{77}$$

$$A(\kappa) = (A_{11}) = \sum_{\nu_2\nu_2'} a_1^*(\nu_2) a_1(\nu_2') \times \int d\kappa' \, \overline{G}_{\nu_2'\nu_2}(\kappa') \, P(\kappa - \kappa') \,, \tag{78}$$

the Dyson equation is

$$\overline{G}_\nu = G^0_\nu(\kappa)\delta_{\nu\nu'} + \frac{G^0_{\nu'}(\kappa) a_1^*(\nu') A(\kappa) a_1(\nu) G^0_\nu(\kappa)}{1 - C^0(\kappa) A(\kappa)} \,. \tag{79}$$

Furthermore, we find

$$C(\kappa) = C^0(\kappa) + C^0(\kappa) A(\kappa) C(\kappa) \,, \tag{80}$$

$$C(\kappa) = \frac{C^0(\kappa)}{1 - C^0(\kappa) A(\kappa)} \,, \tag{81}$$

and

$$A(\kappa) = \int d\kappa' \, \frac{C^0(\kappa') P(\kappa - \kappa')}{1 - C^0(\kappa') A(\kappa')} \,. \tag{82}$$

In this form, Eqs. (80) and (81) are exactly analogous to the equations for the electron Green's function $[C(\kappa)]$ and electron self-energy $[A(\kappa)]$ in the electron-phonon problem $[P(\kappa - \kappa')$ plays the role of the phonon propagator$]$ when vertex corrections are neglected.[24,25] Several important differences exist, however. As previously mentioned, since $D(\kappa) \equiv D(\vec{k}, \omega)$ is assumed known, processes analogous to phonon self-energies in the electron-phonon problem can be neglected. Second, the variable $\kappa \equiv (\vec{k}, \mathcal{E})$ is a three-variable since $\vec{k}$ is a vector parallel to the scattering surface. For phonons in the Einstein and Debye approximations, Engelsverg and Schrieffer[25] solved Eqs. (80) and (82) by using the assumption that the important range in the self-energy integral [in Eq. (82)] is a small interval, of the order of the Debye energy in width, about the Fermi energy. This allowed them to replace the electron density of states by a constant value and, thus, to be able to carry out the integral in (82). Such a procedure is possible here, but its validity is questionable because the relevant atom energies are of the order of the Debye energy rather than the order of the Fermi energy.

In other cases, one is left with the possibility of iterating on the $A(\kappa)$ equation to obtain a continued fractionlike approximation for $A^i(\kappa)$,

$$A^{(1)}(\kappa) = d\kappa' \, C^0(\kappa') P(\kappa - \kappa') \,,$$

$$A^{(n)}(\kappa) = \int d\kappa^1 \, P(\kappa - \kappa^1) \bigg/ \left(C^0(\kappa)^{-1} - \int d\kappa^2 \, \frac{P(\kappa^1 - \kappa^2)}{\ddots} \right) . \tag{83}$$

As before, $A(\kappa) \sim A^{(n)}(\kappa)$ amounts to an n-fluctuation approximation that sums all diagrams with n or less fluctuations existing at the same time and with no lines that cross (no vertex corrections). To derive expressions for cross sections and lifetimes, we will use the one-fluctuation approximation, but the same procedure is applicable for an n-fluctuation approximation so long as vertex corrections are neglected.

IV. T MATRIX; CROSS SECTIONS AND LIFETIMES

To demonstrate the procedure for calculating the inelastic atom-surface scattering, adsorption, and emission cross sections, and decay rates for given states, we start with the results of Sec. III obtained with a factorizable matrix element and the one-fluctuation approximation. The generalization to n fluctuations with the factorizable matrix element is straightforward. The cross sections and lifetimes are obtained from the T matrix, which is given by

$$T^{(1)}_{\nu'\nu}(\kappa) = a_1(\nu) a^*(\nu') [A^{(1)}(\kappa) / \Lambda(\kappa)] \,, \tag{84}$$

where

$$\Lambda(\kappa) = 1 - C^0(\kappa) A^{(1)}(\kappa) \,. \tag{85}$$

The distorted-wave Born approximation result is obtained by replacing $\Lambda(\kappa) = 1$.

The scattering cross section for a transition from state $m \equiv (\vec{k}, \nu)$ to state $m' \equiv (\vec{k}', \nu')$ is related to the imaginary part of T_{mm} by the optical theorem[8]:

$$\sigma_T(m) = -\frac{2}{v_m} (2\pi)^3 \, \mathrm{Im}[T_{mm}(\mathcal{E})] = \sum_{m'} \sigma(m \to m') = \sum_{(\vec{k}', \nu')} \sigma(\vec{k}, \nu \to \vec{k}', \nu') \,. \tag{86}$$

Here $\sigma_T(m)$ is the total scattering cross section for an atom in state m, while $\sigma(m \to m')$ is a differential cross section to scatter from m to m', and v_m is the speed of an atom in state m. The sum over m' includes both discrete and continuum states. The imaginary part of T_{mm} is found by returning to the definitions of $A^{(1)}(\kappa)$ and $C^0(\kappa)$ and writing them in terms of their real and imaginary parts:

$$A_R^{(1)}(\kappa)=\sum_{m_1\equiv\vec{k}_1,\nu_1} P|a_1(\nu_1)|^2\int_0^\infty d\xi \times\left(\frac{1+b(\xi)}{E-\mathcal{E}_{\vec{k}_1,\nu_1}-\xi}+\frac{b(\xi)}{E-\mathcal{E}_{\vec{k}_1,\nu_1}+\xi}\right) D(\vec{q},\xi)\,, \quad (87)$$

$$A_I^{(1)}(\kappa)=-\pi\sum_{m_1\equiv\vec{k}_1,\nu_1}|a_1(\nu_1)|^2\int_0^\infty d\xi\, D(\vec{q},\xi)\{[1+b(\xi)] \times\delta(E-\mathcal{E}_{\vec{k}_1,\nu_1}-\xi)+\delta(E-\mathcal{E}_{\vec{k}_1,\nu_1}+\xi)b(\xi)\}\,. \quad (88)$$

Here, for T on the energy shell, we have $\kappa=(\vec{k},E)$, with $E\equiv\mathcal{E}_{\vec{k},\nu}=k^2/2M+\nu$. The functions $b(\xi)$ are the Bose factors. We can carry out the integrals over ξ in the definition of $A_I^{(1)}(\kappa)$ by setting $\Delta_{\mathcal{E}}\equiv E-\mathcal{E}_{\vec{k}_1,\nu_1}$. Then

$$A_I^{(1)}(\mathcal{E})=-\pi\sum_{\vec{k}_1,\nu_1}|a_1(\nu_1)|^2\{D(\vec{q},\Delta_{\mathcal{E}})[1+b(\Delta_{\mathcal{E}})]H(\Delta_{\mathcal{E}}) + D(\vec{q},-\Delta_{\mathcal{E}})b(-\Delta_{\mathcal{E}})H(-\Delta_{\mathcal{E}})\}\,. \quad (89)$$

The function $H(x)$ is the Heaviside unit step function. The same type of decomposition can be performed for $C^0(\kappa)$ and gives

$$C_R^0(\kappa)=\sum_{\nu_1}|a_1(\nu_1)|^2\frac{P}{\nu-\nu_1}\,, \quad (90)$$

$$C_I^0=-\pi\sum_{\nu_1}|a_1(\nu_1)|^2\delta(\nu-\nu_1)\,. \quad (91)$$

In these equations, the symbol P indicates that a principal-value integral is required.

The expressions (87) and (89)–(91) are now used to express $\Lambda(\kappa)$, defined by Eq. (85), in terms of its real and imaginary parts:

$$\Lambda_R(\kappa)=1-[C_R^0(\kappa)A_R^{(1)}(\kappa)-C_I^0(\kappa)A_I^{(1)}(\kappa)]\,, \quad (92)$$

$$\Lambda_I(\kappa)=C_I^0(\kappa)A_R^{(1)}(\kappa)+C_R^0(\kappa)A_I^{(1)}(\kappa)\,. \quad (93)$$

With these definitions, the cross section in Eq. (86) has the compact form

$$\sigma(m)=-2\frac{(2\pi)^3}{v_m}\mathrm{Im}(T_{mm}^{(1)})=-16\pi^3\frac{|a_1(\nu)|^2}{v_m} \times\frac{A_I^{(1)}(\kappa)\Lambda_R(\kappa)+A_R^{(1)}(\kappa)\Lambda_I(\kappa)}{[\Lambda_R(\kappa)]^2+[\Lambda_I(\kappa)]^2}\,. \quad (94)$$

The differential cross section $\sigma(m\to m_1)$ is found by replacing $A_I^{(1)}$ and $A_R^{(1)}$ in the numerator of Eq. (94) with their definitions (87) and (89) without the sum over final states:

$$\sigma(m\to m_1)\equiv\sigma(\vec{k},\nu\to\vec{k}_1,\nu_1)=16\pi^3\frac{|a_1(\nu)a_1(\nu_1)|^2}{v_m} \times\left(\frac{\rho(\vec{k}_1)\,\rho(\nu_1)}{\Lambda_R(\kappa)^2+\Lambda_I(\kappa)^2}\right)B(\kappa,\vec{q},\Delta_{\mathcal{E}})\,, \quad (95)$$

where

$$B(\kappa,\vec{q},\Delta_{\mathcal{E}})\equiv\Big[\pi\Lambda_R(\kappa)\{D(\vec{q},\Delta_{\mathcal{E}})[1+b(\Delta_{\mathcal{E}})]H(\Delta_{\mathcal{E}}) + D(\vec{q},-\Delta_{\mathcal{E}})b(-\Delta_{\mathcal{E}})H(-\Delta_{\mathcal{E}})\} - \Lambda_I(\kappa)\int_0^\infty d\xi\, D(\vec{q},\xi)\left(\frac{1+b(\xi)}{\Delta_{\mathcal{E}}-\xi}+\frac{b(\xi)}{\Delta_{\mathcal{E}}+\xi}\right)\Big]\,. \quad (96)$$

The factors $\rho(\vec{k}_1)$ and $\rho(\nu_1)$ represent the density of $\vec{k}_1$ states and ν_1 states, respectively, i.e., a density of final states. The DWBA result is obtained by letting $\Delta_R\to1$ and $\Lambda_I\to0$, namely,

$$\sigma(m\to m_1)\equiv\sigma(\vec{k},\nu\to\vec{k}_1,\nu_1)=16\pi^3\frac{|a_1(\nu)a_1(\nu_1)|^2}{v_m} \times\rho(\vec{k}_1)\rho(\nu_1)\{D(\vec{q},\Delta_{\mathcal{E}})[1+b(\Delta_{\mathcal{E}})]H(\Delta_{\mathcal{E}}) + D(\vec{q},-\Delta_{\mathcal{E}})b(-\Delta_{\mathcal{E}})H(-\Delta_{\mathcal{E}})\}\,. \quad (97)$$

We recover the exact second-order result by replacing $|a_1(\nu)a_1(\nu_1)|^2$, the square of the matrix element, by $|M_{\nu_1\nu}|^2$.

Equation (97) is in close analogy with the basic cross-section equation for the scattering of neutrons from a system of interacting particles as derived by Van Hove.[29] Van Hove expresses the scattering cross section in terms of the Fourier transform of the space-time pair distribution function. The analogy is most easily seen by relating, term by term, the quantities in Eq. (97) to those in the equation for the neutron scattering cross section. Using the symbol $\longleftarrow$ to denote "analogous to," the notation of Van Hove,[29] and the variable $\eta=k^2/2M$, we find, first,

$$\rho(\eta)\rho(\nu)/v_m\longleftarrow k/k_0\,. \quad (98)$$

The numerators are from density-of-states factors, while the denominators are the result of dividing by the incident flux. Second, the analogy of matrix elements is

$$|M_{\nu_1\nu}|^2 \text{ or } |a_1(\nu)a_1^*(\nu_1)|^2\longleftarrow W(\kappa)\equiv V_{kk_0}^2 =[\textstyle\int e^{i\vec{\kappa}\cdot\vec{r}}V(\vec{r})\,d\vec{r}]^2. \quad (99)$$

Finally,

$$D(\vec{q},\Delta_{\mathcal{E}})\longleftarrow S(\vec{q},\omega), \quad (100)$$

so that the Fourier transform of the fluctuation-correlation function plays a role analogous to the Fourier transform of the generalized pair distribution function.

Equations (94) and (95), for $\sigma(m)$ and $\sigma(m\to m_1)$, differ from the Born approximation expressions in that they contain the characteristic denominator $\Lambda_R^2(\kappa)+\Lambda_I^2(\kappa)$ which results from summing all one-fluctuation diagrams to infinite order in the perturbation series expansion. A characteristic resonance line shape for the inelastic atom-scattering cross section will result if $\Lambda_I(\kappa)$ is smoothly varying in the vicinity of a zero of $\Lambda_R(\kappa)$. Furthermore, this characteristic form of the denominator will result at every order of approximation to $A(\kappa)$. In particular, at nth order, where nth-order fluctuation processes are included, but vertex corrections are neglected, we simply replace, in Eqs. (92) and (93), $A_R^{(1)}(\kappa)$ by $A_R^{(n)}(\kappa)$ and $A_I^{(1)}(\kappa)$ by $A_I^{(n)}(\kappa)$. Whether or not a resonance point is shifted in higher-order approximations depends on the convergence properties of the iteration scheme. A specific example will be discussed in Sec. V.

A quantity of special interest is the adsorption or capture cross section for the capture of an atom by the fluctuating surface field. In such a reaction, the particle makes a transition between a state $(\vec{k}, \nu)$, for ν in the continuum (denoted $\nu \in C_\nu$), to a state $(\vec{k}_1, -\nu_B)$, where ν_B is the energy of a discrete bound state. Let S_ν denote the complete set of ν states, discrete plus continuum, and D_ν the set of discrete states only. Then the capture cross section for an incident atom in state $m \equiv (\vec{k}, \nu)$ is

$$\sigma_{\text{ads}}(m) = \sum_{\vec{k}_1, \nu_1 \in D_\nu} \left(\frac{16\pi^3 |a_1(\nu) a_1(\nu_1)|^2 \rho(\vec{k}_1)}{(v_{\vec{k}_1\nu}) \{ [\Lambda_R(k_1\nu)]^2 + [\Lambda_I(k_1\nu)]^2 \}} \right) \times B(m, \vec{q}, \Delta_{\mathcal{E}}) . \quad (101)$$

In the special case of a single bound state of energy $(-\nu_B)$, $\nu_B > 0$, we delete the sum over D_ν and replace ν_1 by $-\nu_B$.

For a beam of atoms incident on a surface, we can define an average adsorption or capture cross section by summing $\sigma(m) \equiv \sigma(\vec{k}, \nu)$ over all $\vec{k}$ and $\nu \in C_\nu$ using a weighting function $P(m)$, the probability that an atom in the incident beam is in state m. Thus

$$\langle \sigma_{\text{ads}} \rangle = \sum_{\substack{m \\ \nu \in C_\nu}} P(m) \sigma_{\text{ads}}(m) . \quad (102)$$

An average total cross section is defined in a similar manner. The total cross section is

$$\sigma_T(m) = \sum_{\substack{\vec{k}_1 \\ \nu_1 \in S_\nu}} \left(\frac{16\pi^3 |a_1(\nu) a_1(\nu_1)|^2 \rho(k_1) \rho(\nu_1)}{(v_{k_1, \nu_1}) [\Lambda_R(k_1\nu)^2 + \Lambda_I^2(k_1\nu)]} \right) \times B(m, \vec{q}, \Lambda_{\mathcal{E}}) , \quad (103)$$

so that

$$\langle \sigma_T \rangle = \sum_{\substack{m \\ \nu \in C_\nu}} P(m) \sigma_T(m) . \quad (104)$$

The ratio $\sigma_{\text{ads}}(m)/\sigma_T(m)$ is the condensation coefficient for an atom in state m and the ratio of the average values,

$$\bar{\sigma}_c = \langle \sigma_{\text{ads}} \rangle / \langle \sigma_T \rangle \leq 1 , \quad (105)$$

is an expression for the standard definition[30] of a condensation coefficient. $\bar{\sigma}_c$ is of importance for problems in gas dynamics,[12] boiling and cavitation phenomena,[31] film condensation,[32] etc., aside from being an intrinsic characteristic of the surface field.

In a completely analogous fashion, an expression can be derived for an emission or desorption cross section. We note here that, even at $T = 0$, decay of the bound state into the continuum (desorption) is possible for a large enough energy component parallel to the surface. Figure 1 illustrates this possibility for the case of a single bound state. The threshold wave vector is given by $|k_{\text{th}}| = 2M\nu_B$, where M is the mass of the incident atom. For $|k| > |k_{\text{th}}|$, decay is possible by emission of a surface fluctuation. A simple example is given in the next section for the lifetime of the bound state based upon models of the fluctuation-correlation function.

V. SIMPLE MODELS AND ILLUSTRATIVE EXAMPLES

To simply illustrate the formalism, we present here a simple mean potential field that leads to a separable matrix element which is used in conjunction with models of the fluctuation-correlation function to perform a demonstrative calculation of the lifetime of a bound state and to investigate the existence of scattering resonances. The latter entails a brief examination of the properties of the functions $\Lambda_r(\kappa)$ and $\Lambda_I(\kappa)$ in Eqs. (92) and (93), respectively.

Consider first approximating the mean potential field $V_0(z)$ by a square well:

$$V_0(z) = \begin{cases} \infty , & z < 0 \\ -s , & 0 < z < z_0 \\ 0 , & z_0 < z . \end{cases} \quad (106)$$

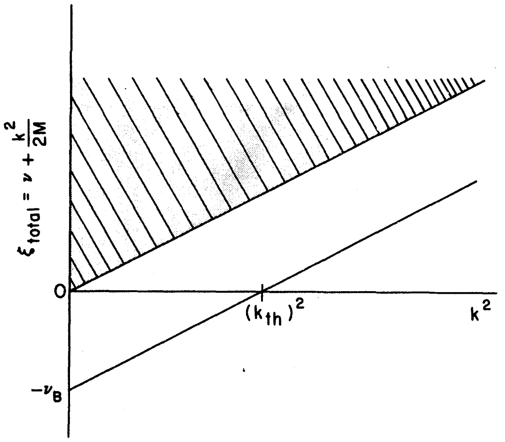


FIG. 1. Illustration of the variation of the total energy as a function of the square of the wave vector of the atom parallel to the surface. ν is a parameter on this graph and, for simplicity, only a single bound state of energy ν_B is shown. All $\nu \in [0, \infty]$ are also possible. Note that at $T = 0$, decay of a particle from the bound state to a continuum state in ν is possible only for $k^2 > k_{\text{th}}^2$.

The eigenfunctions $\varphi_\nu(z)$ of H_0 are nonzero in the half-space $z > 0$ and satisfy the boundary condition

$$\varphi_\nu(0) = 0 \ . \tag{107}$$

Thus, the matrix element $M_{\nu'\nu}$, defined by

$$M_{\nu'\nu} = \int_0^\infty dz\, \varphi_{\nu'}^*(z) \frac{\partial V}{\partial z}\, \varphi_\nu(z) \ , \tag{108}$$

becomes

$$M_{\nu'\nu} = s\varphi_\nu(z_0)\, \varphi_{\nu'}^*(z_0) \ , \tag{109}$$

which is separable in ν and ν' and depends in a straightforward way on the strength s and range z_0 of the mean potential field. In the previous notation, therefore, we define

$$a_1(\nu) = s^{1/2}\varphi_\nu(z_0) \ . \tag{110}$$

To proceed further, we also require a form for the Fourier transform of the fluctuation-correlation function $D(\vec{q}, \omega)$ (recall that $\vec{q}$ is a two-dimensional vector in the plane of the surface). Two simple models that can be used are

$$D(\vec{q}, \omega) = \mathcal{A}\,\delta(\omega - \omega(\vec{q})) \ . \tag{111}$$

which corresponds to phonons on the surface, and

$$D(\vec{q}, \omega) = (Dq^2 + \Gamma)/[(Dq^2 + \Gamma)^2 + \omega^2] \ , \tag{112}$$

which results from making a Gaussian approximation for the correlation function $D(\vec{x}, \tau)$. The factor Γ represents a finite lifetime for the correlation between fluctuations. The latter approximation can be appropriate for a liquid surface.

As a simplest example of the use of Eqs. (109), (111), and (112), consider the calculation of the lifetime of a bound state (lifetime of a particle adsorbed on the surface) at $T = 0$ using second-order perturbation theory. The lifetime exhibits a threshold in k^2, as illustrated in Fig. 1, and we consider the case of a single bound state. The formula for the lifetime is

$$\frac{1}{\tau_{\vec{k},\nu_B}} = -2\,\mathrm{Im}\,[T_{\nu_B\nu_B}(\vec{k})] = -2 \sum_{\substack{\vec{k}_1,\nu_1\\ \nu_1 \in C_\nu}} s^2 |\varphi_{\nu_1}(z_0)\varphi_{\nu_B}(z_0)|^2 \times \mathrm{Im}\int_0^\infty d\xi\, \frac{D(\vec{q}, \xi)}{\mathcal{E}_{\vec{k},\nu_B} - \mathcal{E}_{\vec{k}_1,\nu_1} - \xi + i\delta} \ . \tag{113}$$

Converting sums to integrals and denoting density-of-state functions by ρ, we find

$$\frac{1}{\tau_{\vec{k},\nu_B}} = 2\pi s^2\, |\varphi_{\nu_B}(z_0)|^2 \iint \rho(\vec{k}_1)\, d\vec{k}_1 \rho(\nu_1) d\nu_1 |\varphi_{\nu_1}(z_0)|^2 \times D(\vec{q}, \mathcal{E}_{\vec{k},\nu_B} - \mathcal{E}_{\vec{k}_1,\nu_1}) \ . \tag{114}$$

For phonons in the Einstein approximation, the angular dependence becomes trivial and the lifetime is

$$\frac{1}{\tau_{\vec{k},\nu_B}} = 2\pi s^2\, |\varphi_{\nu_B}(z_0)|^2\, H[k^2 - (k_{\mathrm{th}})^2]\mathcal{A} \int_0^{\nu_{\max}} d\nu_1 \times \rho(\nu_1) |\varphi_{\nu_1}(z_0)|^2 \ . \tag{115}$$

The Heaviside step function $H(k^2 - (k_{\mathrm{th}})^2)$ recalls the fact that decay is not possible unless k^2 is greater than a threshold value $(k_{\mathrm{th}})^2$ as illustrated in Fig. 1. The upper limit $\nu_{\max}$ is

$$\nu_{\max} = (k^2/2M - \nu_B) - \omega_0 \ , \tag{116}$$

where M is the mass of the adsorbed particle and ω_0 is the Einstein frequency. Note that the lifetime is independent of $\vec{k}$ except for the threshold condition $k^2 > (k_{\mathrm{th}})^2$.

When the Gaussian approximation is used, the integrals become somewhat more involved because of the nontrivial angular integral. However, for $|\vec{k}|$ near $|\vec{k}_{\mathrm{th}}|$, we can expand $D(\vec{q}, \Lambda_{\mathcal{E}})$, $\Delta_{\mathcal{E}} \equiv \mathcal{E}_{\vec{k},\nu_B} - \mathcal{E}_{\vec{k}_1,\nu_1}$ for $|\vec{q}| \simeq k_{\mathrm{th}}$, $\Delta_{\mathcal{E}} \simeq 0$. Since $D(\vec{q}, \Delta_{\mathcal{E}})$ depends only on $\vec{q}^2$, define $D(\vec{q}, \omega) \equiv D(q, \omega)$ and write

$$D(q, \omega) = D(k_{\mathrm{th}}, 0) + \left.\frac{\partial D}{\partial q}\right|_{q = k_{\mathrm{th}}} (q - k_{\mathrm{th}}) + \left.\frac{\partial D}{\partial \Delta_{\mathcal{E}}}\right|_{\Delta_{\mathcal{E}} = 0} \Delta_{\mathcal{E}} + \cdots \ . \tag{117}$$

Retaining only the zeroth-order term leads to

$$\frac{1}{\tau_{\vec{k},\nu_B}} \simeq \frac{(2\pi s^2)\, |\varphi_{\nu_B}(z_0)|^2}{(Dk_{\mathrm{th}}^2 + \Gamma)} \iint d\vec{k}_1\, d\nu_1 \times \rho(\vec{k}_1)\, \rho(\nu_1) |\varphi_{\nu_1}(z_0)|^2 \ , \tag{118}$$

and, since the range of the ν_1 integral is small,

$$\frac{1}{\tau_{\vec{k},\nu_B}} \simeq \frac{(2\pi s^2)\, |\varphi_{\nu_B}(z_0)|^2\, |\varphi_{\nu=0}(z_0)|^2\, N_T(\nu_B + k^2/2M)}{D(k_{\mathrm{th}})^2 + \Gamma} \ . \tag{119}$$

The function

$$N_T(\nu_B + k^2/2M) \equiv \int\int \rho(\vec{k}_1)\, d\vec{k}_1\, \rho(\nu_1)\, d\nu_1 \tag{120}$$

is the total number of states in $(\vec{k}_1, \nu_1)$ space satisfying the conditions

$$\nu_1 \in [0, (k_1)^2_{\max}/2M] \ , \qquad (k_1)^2 \in [0, (k_1)^2_{\max}] \ ,$$

with $(k_1)^2_{\max}$ defined by

$$(k_1)^2_{\max} = k^2 - 2M\nu_B \ . \tag{121}$$

Thus, N_T is the total number of states available to an atom decaying from the bound state $(\vec{k}, \nu_B)$. Again, Eq. (119) is valid for k^2 in the vicinity of the threshold $(k_{\mathrm{th}})^2 = 2M\nu_B$.

To illustrate the formulas required to investigate the existence of resonance points in the inelastic scattering cross section, consider the functions $\Lambda_R(\kappa)$ and $\Lambda_I(\kappa)$ as defined in Eqs. (94) and (95), respectively, and consider the phonon model of $D(\vec{q}, \omega)$ in the Einstein approximation. At $T = 0$, the pertinent formulas are (for $\nu \in C_\nu$)

$$A_R^{(1)}(\vec{k},\nu)=s\,|\varphi_{\nu_B}(z_0)|^2\int d\eta_1\rho(\eta_1)\,\frac{\mathcal{A}}{\nu+\nu_B+\eta-\eta_1-\omega_0}+s\iint d\eta_1\,d\nu_1\,\rho(\eta_1)\rho(\nu_1)\,|\varphi_{\nu_1}(z_0)|^2\,\frac{\mathcal{A}}{(\nu-\nu_1)+(\eta-\eta_1)-\omega_0}, \tag{122}$$

$$A_I^{(1)}(\vec{k},\nu)=-\pi s\,|\varphi_{\nu_B}(z_0)|^2\mathcal{A}\int d\eta_1\,\rho(\eta_1)\,\delta(\nu+\eta+\nu_B-\eta_1-\omega_0) \\ -\pi s\,\mathcal{A}\int d\eta_1\,d\nu_1\,\rho(\eta_1)\rho(\nu_1)\,|\varphi_{\nu_1}(z_0)|^2\,\delta(\nu-\nu_1+\eta-\eta_1-\omega_0)\,, \tag{123}$$

$$C_R^0(\eta,\nu)=s\left(\frac{|\varphi_{\nu_B}(z_0)|^2}{\nu+\nu_B}+-\!\!\!\!\!\!\int_0^\infty\frac{d\nu_1\rho(\nu_1)\,|\varphi_{\nu_1}(z_0)|^2}{\nu-\nu_1}\right)\,, \tag{124}$$

and

$$C_I^0(\eta,\nu)=-\pi s\,\rho(\nu)\,|\varphi_\nu(z_0)|^2\,,\quad \nu\in C_\nu\,. \tag{125}$$

We have restricted ourselves to the case of a single bound state ν_B and are interested in examining whether or not the function $\Lambda_R(\vec{k},\nu)$, defined as

$$\Lambda_R(\vec{k},\nu)=1+C_I^0(\eta,\nu)A_I^{(1)}(\eta,\nu)-C_R^0(\eta,\nu)A_R^{(1)}(\eta,\nu)\;, \tag{126}$$

can have zeros. Since $C_I^0(\eta,\nu)A_I^0(\eta,\nu)\geq 0$ for all η and ν, the product $C_R^0A_R^{(1)}$ must become positive and equal to $1+C_I^0A_I^{(1)}$ at some (η,ν). In the limit that $\nu\to\infty$, $A_R^{(1)}$ and C_R^0 both tend to zero, while at $(\eta,\nu)=(0,0)$, the sign of $A_R^{(1)}C_R^0$ is determined by the parameters ν_B, ω_0 and the matrix elements. In addition, both $C_I^0A_I^{(1)}$ and $C_R^0A_R^{(1)}$ are proportional to s^2, the square of the well depth. Thus, a surface whose attractive field strength is too weak will not exhibit resonance points. It is clear, therefore, that the zeros of $\Lambda_R(\kappa)$ are intimately related to the gross properties of the surface (namely, ν_B, s, and z_0). In detailed calculations, one would use a more realistic surface field, such as that used by Cabrera, Celli, and Manson,[6,9] and a model of the fluctuation-correlation function most appropriate to the surface under study. Alternatively, a realistic potential field and experimental results can be used together to derive information regarding the correlations of the surface excitations.

VI. DISCUSSION

The approach to inelastic atom-surface scattering developed in the preceding sections provides an adequate means for investigating surfaces that can be treated in the continuum approximation. These include liquids, amorphous solids, and crystalline solids when surface-diffraction effects are neglected. Atom scattering is particularly useful for studying surface effects, since the atoms interact primarily with the surface field rather than, as with penetrating radiation such as neutrons, with the bulk medium.

To compare some of the approximate results discussed herein with experimental data, one must perform calculations with a more realistic form of the mean potential field (and its associated eigenfunctions) than the simple square well discussed in Sec. V. Such a comparison can test the adequacy of a one or more fluctuation approximation and, perhaps, the effects of neglecting higher-order vertex corrections. Alternatively, experimental results can be used in conjunction with an adequate mean surface field to deduce results concerning the fluctuation-correlation function.

A further investigation of the characteristic resonancelike form of the inelastic-scattering cross section as given in Eq. (95) can prove fruitful in providing information about the parameters which characterize the mean surface field (such as strength and range.) The characteristic denominators are absent in lowest-order perturbation theory.

The theory as developed can also apply to scattering of atoms from a surface covered with impurities if one treats the diffusive motion of the impurities as a stochastic process. Assuming the impurity particles' motion, averaged over a statistical ensemble, can be characterized as a Gaussian random process (also called a multivariate normal process), the theory as developed will apply.

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APPENDIX

In this Appendix, a derivation is given for the temperature-dependent coefficient $V_1(z,T)$ of $\delta R(\vec{x})$ as used in Eq. (10) of the text. In essence, a renormalized harmonic approximation or renormalized vertex is used to relieve the restriction of small amplitude $\delta R(\vec{x})$.

Begin by writing down the power-series expansion:

$$V(z,\delta R)=V_0(z)+V^{(1)}(z)\delta R(\vec{x},t) \\ +\frac{V^{(2)}(z)}{2!}\,\delta R^2(\vec{x},t)+\cdots\;. \tag{A1}$$

As before, $V^{(n)}(z)$ denotes the nth derivate and $V_0(z)$ is the mean potential field of the surface. Thus, the perturbing Hamiltonian is defined by

$$\mathcal{H}_1(\vec{r},t)=V^{(1)}(z)\delta R(\vec{x},t)+\frac{V^{(2)}(z)}{2!}\,\delta R^2(\vec{x},t)+\cdots\;. \tag{A2}$$

To approximately sum this series, we make a renormalized harmonic approximation. To do this, write

$$\delta R^{n+1} = (\delta R^n(\vec{x}, t))\,\delta R(\vec{x}, t) \tag{A3}$$

and approximate (δR^n) by n times its equal space-time average, i.e.,

$$\delta R^n(\vec{x}, t) = n\,\langle \delta R^n \rangle\,, \quad n = 1, 2, \ldots . \tag{A4}$$

Furthermore, assuming

$$\langle \delta R \rangle = 0 \tag{A5}$$

and

$$\langle \delta R^{2n+1} \rangle = 0\,, \tag{A6}$$

$\mathcal{H}_1(\vec{r}, t)$ becomes

$$\mathcal{H}_1(\vec{r}, t) = \left\langle \frac{\partial}{\partial z}\left(1 + \frac{(\delta R)^2}{2!}\frac{\partial^2}{\partial z^2} + \frac{(\delta R)^4}{4!}\frac{\partial^4}{\partial z^4} + \cdots\right) V(z)\right\rangle \times \delta R(\vec{x}, t)\,. \tag{A7}$$

Summing the series inside $\langle \cdots \rangle$ yields

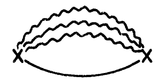
$$\mathcal{H}_1(\vec{r}, t) = \left\langle \frac{\partial}{\partial z}\left[\cosh\left(\delta R\,\frac{\partial}{\partial z}\right) V(z)\right]\right\rangle \delta R(\vec{x}, t)\,. \tag{A8}$$

Writing the average in terms of the trace over $e^{-\beta H_a}$, where H_a is the adsorbate Hamiltonian, the coefficient of $\delta R(\vec{x}, t)$ is

$$V_1(z, T) = Z^{-1}\,\mathrm{tr}\left\{e^{-\beta H_a}\,\frac{\partial}{\partial z}\left[\cosh\left(\delta R\,\frac{\partial}{\partial z}\right)\right] V(z)\right\}\,, \tag{A9}$$

$$Z = \mathrm{tr}(e^{-\beta H_a})\,. \tag{A10}$$

Note that the renormalized harmonic approximation amounts to using a renormalized vertex. That is, one replaces multifluctuation processes, such as

 (A11)

by a renormalized vertex, e.g.,

 . (A12)

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